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IT-5-P-2963 TEM-EELS/SXES studies on electronic structures of p-type CaB₆

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Metal hexaboride MB₆ is based on a network of B₆-clusters located on each corner of cubic unit cell. M atom occupies at the body center position of the unit cell. When an M atom can supply two electrons to B₆-network, the valence bands (VB) of this material is fully occupied and becomes a semiconductor. Those semiconductor materials have been investigated as a candidate for a high-temperature thermoelectric-power material. Seebeck coefficients of MB₆ (M=Ba, Sr, Ca) synthesized by solid-state reaction method were reported to be negative, indicating those are n-type materials [1]. Recently, the p-type character for CaB₆ synthesized from the mixture of CaCl₂ and NaBH₄ in eutectic LiCl-KCl molten salt was reported [2]. Thus, the electronic structure of this new material has been studied by using electron energy-loss spectroscopy (EELS) [3] and soft-X-ray emission spectroscopy (SXES) [4], which are methods for probing over and below the Fermi energy level, respectively.

EDS analysis of the p-type CaB₆ showed an inclusion of a few % of Na. Electron diffraction patterns showed a good crystalline order. As one Na atom can transfer one electron to B₆-network, Na-doping can be a hole-doping based on the rigid band structure scheme when doped Na atoms occupy Ca site. Valence electron excitation (from VB to conduction bands: CB) EELS spectra showed smaller bandgap energy of 1.5 eV than 2.5 eV of n-type CaB₆ synthesized by solid-state reaction method. B K-shell excitation EELS spectra of p- and n-type materials showed almost the same onset energy, which energy position corresponds to the bottom of CB.

Figure 1 shows B K-emission SXES spectra of p-type and n-type CaB₆. Those spectra show different intensity distribution especially at the top region of VB, which correspond to the right hand side end of the intensity distribution. The intensity distribution of p-type material apparently extends into the bandgap region of n-type CaB₆. Since the bottom of CBs of the two materials were the same, this higher energy position of the top of VB of p-type should be the origin of the smaller bandgap energy of p-type material. This is consistent with the result of valence excitation EELS experiment stated above. This indicates that the doping of Na atoms into the Ca site of CaB₆ causes not only the creation of holes in VB but also a change the energy state at the top region of VB, not a simple rigid band structure scheme.

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[2] K.Inayoshi and M. Takeda, IUMRS-ICEM (2012).

[3] Y.Sato et al., Ultramicroscopy 111, 1381-1387 (2011)

[4] M.Terauchi et al, Journal of Electron Microscopy 61, 1-8 (2012).

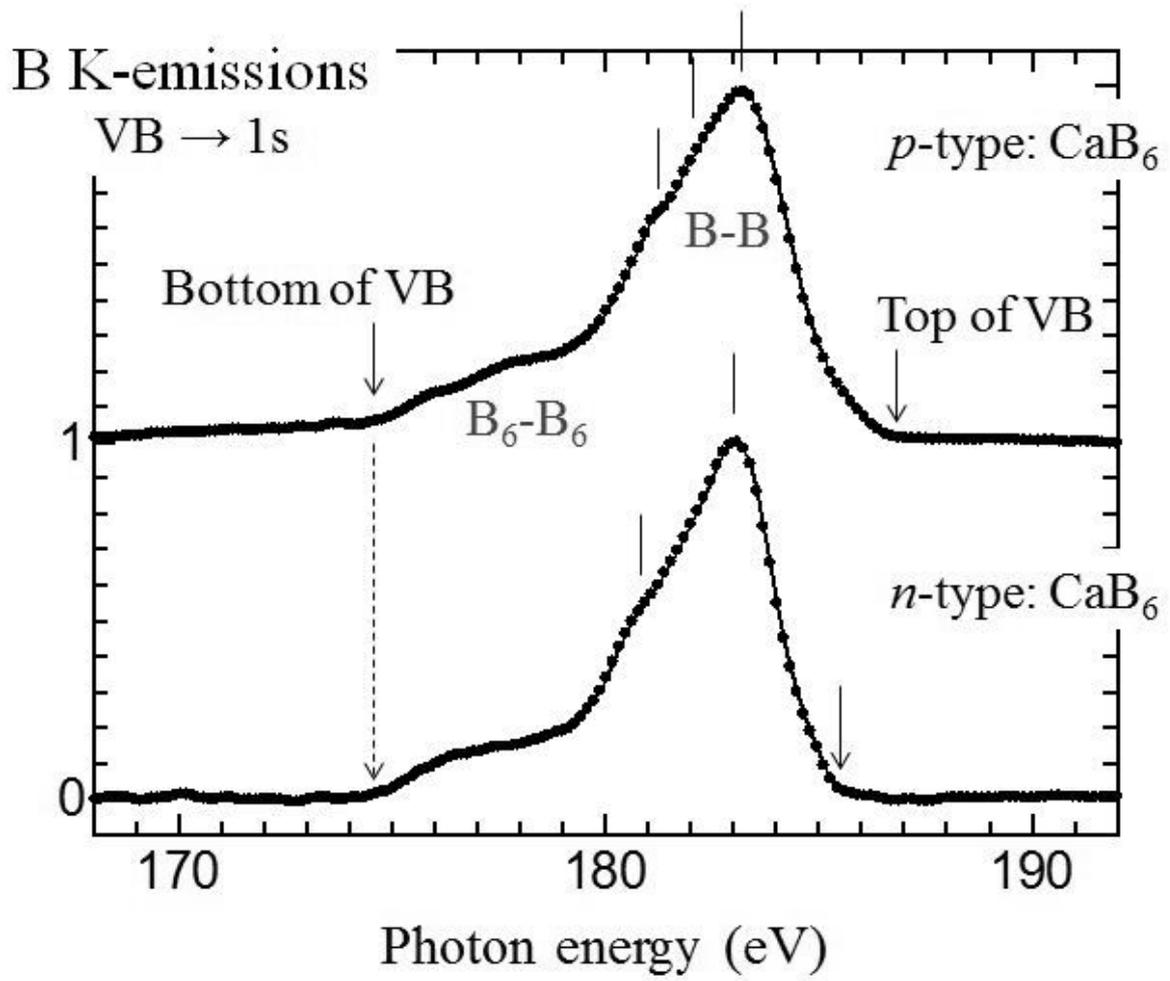


Fig. 1: B K-emission SXES spectra of *p*-type and *n*-type CaB_6 .